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# Inner and outer radial density functions in correlated two-electron systems

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A method is presented for determining inner- and outer-electron radial density functions for two-electron systems by partitioning the fully correlated, two-electron, radial density function. This is applied to the helium isoelectronic series ( $Z = 1$  to 10 and 100) and the critical nuclear charge system, which has the minimum charge for which the atomic system has at least one bound state, to separate out the motions of the two electrons in both weakly and strongly bound systems. It is found that the inner electron experiences a negative screening effect due to the perturbation by the other electron. This is quantified and shown to increase with increasing  $Z$ . For the weakly bound systems the inner radial density distribution closely resembles that of a hydrogenic atom with the outer radial density distribution becoming very diffuse.

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## I. INTRODUCTION

The accurate treatment of electron correlation, the instantaneous interaction between electrons, is essential for determining accurate atomic and molecular energies. In the early days of quantum mechanics, Hylleraas demonstrated that very accurate nonrelativistic ground-state energies of two-electron atoms were obtainable by direct inclusion of the interelectronic distance  $r_{12}$  in the wave function [1,2]. He constructed a wave function involving what are now known as Hylleraas co-ordinates,  $s = r_1 + r_2$ ,  $t = -r_1 + r_2$ , and  $u = r_{12}$ , where  $r_1$  and  $r_2$  are the nucleus-electron distances and  $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$  is the interelectronic distance. He showed that this approach, which accounts explicitly for correlations between the motion of the two electrons through the variable  $u = r_{12}$ , is very successful at obtaining accurate values of the ground-state energy of the Schrödinger equation for two-electron atoms. However, it was soon realized that direct inclusion of the electron-electron distance is only practicable for systems with few electrons. Instead, more tractable wave functions which do not involve explicitly the interelectronic coordinate have been the primary focus of developments. The starting point is usually Hartree-Fock (HF) theory, which is based on a single-particle model in which each electron moves in an effective potential, and which includes the effect of the average repulsion from the other electrons, and the wave function is an antisymmetrized product of one-electron orbitals. In fact, electron correlation  $E_{\text{corr}}$  is usually defined as the difference between the exact nonrelativistic energy and the nonrelativistic HF energy, and is treated by mixing excited configurations into the HF wave function [3].

However, a HF wave function does not include the Coulomb correlation. The electrons try to avoid each other thus creating what is often referred to as a Coulomb hole around each electron in the atom. For example, in a two-electron atom such as helium, if one electron is close to the nucleus at a given instant, it is energetically favorable for the other electron to be far from the nucleus at that instant. In this paper, we use this principle to partition the two-electron (fully correlated) radial density function into two one-electron components by

defining an *inner* probability density which represents the electron that is closer to the nucleus at a given instant, and an *outer* probability density that represents the electron that is farthest from the nucleus. Thus we determine the probability of an electron being at all radial distances greater than the first to form an inner electron and an outer electron probability distribution.

In a series of papers, Koga and Matsuyama have calculated inner and outer radial density functions in many-electron atoms by rigorously separating the radial density function into an inner and outer component with the use of the Heaviside function [4,5]. Koga has also calculated the average inner and outer radii of two electrons in the ground state of many-electron atoms using the multiconfigurational Hartree-Fock method, and tabulates inner and outer  $\langle r \rangle$  for  $\text{H}^-$  to  $\text{B}^{3+}$  using numerical Hartree-Fock wave functions [6].

In the present work, we use a fully correlated method from the outset by explicitly including the electron-electron distance  $r_{12}$ . All-particle calculations are performed, i.e., electrons and nuclei are treated on an equal footing and so nuclear motion is automatically included. However, the standard clamped nucleus calculations can easily be performed by simply setting the nuclear mass to infinity. The fully correlated radial density function is partitioned into an inner electron and an outer electron component using the sifting property of the Dirac  $\delta$  distribution. The radial density functions that result from the partitioning are used to determine the electron distributions as the nuclear charge increases to determine how correlated systems subtly balance maximizing nuclear-electron attraction while minimizing electron-electron repulsion. This approach is then applied to a two-electron system with the minimum nuclear charge  $Z_C$  required for a bound state to exist (see [7] and references therein) to determine quantitatively the electron distribution just prior to electron attachment.

The critical nuclear charge  $Z_C$  for which a two-electron atom with an infinitely heavy nucleus remains stable has been investigated by several authors. In 2014, Estienne *et al.* [8] calculated a definitive value for the infinite nuclear mass case of  $Z_C = 0.911\,028\,224\,077\,255\,73(4)$ , later confirmed by Pilón and Turbiner [9], and explored the electronic structure near the critical nuclear charge by calculating the radial electron density distribution function. Recently the present authors [7] determined the critical nuclear charge  $Z_C$  for binding of two

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electrons with (i) infinite nuclear mass, reporting a value of  $Z_C = 0.911\,028\,2(3)$  in good agreement with recent literature values, and (ii) explicit consideration of nuclear motion using a range of finite nuclear masses; these values will be used in the present work.

## II. PARTITIONING OF THE TWO-ELECTRON RADIAL DENSITY FUNCTION

The probability density of selected particles in an  $n$ -particle system, measured with respect to some point  $P$  fixed to the body, is [10]

$$D_{P,a_1,a_2,\dots,a_n}^{(n)}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_n) = \langle \psi | \delta(\mathbf{x}_{a_1} - \mathbf{x}_P - \mathbf{R}_1) \delta(\mathbf{x}_{a_2} - \mathbf{x}_P - \mathbf{R}_2) \cdots \times \delta(\mathbf{x}_{a_n} - \mathbf{x}_P - \mathbf{R}_n) | \psi \rangle, \quad (1)$$

where  $\mathbf{R}_i \in \mathbb{R}$  and  $\delta(z)$  is the three-dimensional Dirac delta distribution. The one-particle density function

$$D_{P,a_1}^{(1)}(\mathbf{R}_1) = \langle \psi | \delta(\mathbf{x}_{a_1} - \mathbf{x}_P - \mathbf{R}_1) | \psi \rangle \quad (2)$$

characterizes the spatial distribution of particle  $a_1$  with respect to the center point  $P$ , which in this work is taken to be the center of mass. The two-particle density function

$$D_{P,a_1,a_2}^{(2)}(\mathbf{R}_1, \mathbf{R}_2) = \langle \psi | \delta(\mathbf{x}_{a_1} - \mathbf{x}_P - \mathbf{R}_1) \delta(\mathbf{x}_{a_2} - \mathbf{x}_P - \mathbf{R}_2) | \psi \rangle \quad (3)$$

characterizes the spatial distribution of particles  $a_1$  and  $a_2$  simultaneously, with respect to the center of mass.

In the present work, a body-fixed approach [11] is taken to solving the three-body problem  $\{a_1, a_2, a_3\}$  where  $a_1$  and  $a_2$  are electrons and  $a_3$  is a nucleus of mass  $M$  and charge  $Z$  [12]. Translationally invariant coordinates relative to the center of mass, which in this case coincides with the nucleus, are defined as

$$\mathbf{t}_i = (\mathbf{x}_{a_i} - \mathbf{x}_P), \quad i = 1, 2. \quad (4)$$

The three internal coordinates are invariant under orthogonal transformation of the translation-free coordinates, and following Hylleraas, the internal coordinates are initially chosen as the interparticle distances  $r_1$ ,  $r_2$  and  $r_{12}$  defined as

$$r_i = |\mathbf{t}_i|, \quad i = 1, 2 \quad \text{and} \quad r_{12} = |\mathbf{t}_1 - \mathbf{t}_2|$$

For states with angular momentum  $L = 0$  and parity  $p = +1$ , the wave functions, and thus the particle densities, are spherically symmetric. Therefore  $D_{P,a_1}^{(1)}(\mathbf{R}_1)$  and  $D_{P,a_1,a_2}^{(2)}(\mathbf{R}_1, \mathbf{R}_2)$  are spherically symmetric and their values depend only on the lengths. Following [10], as the overall space rotation inversion leaves the system invariant ( $L = 0$ ,  $p = +1$ ), we can introduce

$$\rho_1(r) = D_{P,a_1}^{(1)}(\mathbf{R}_1), \quad (5)$$

where  $r = |\mathbf{R}_1|$  and  $r \in \mathbb{R}_0^+$ . Throughout this work the radial densities are normalized to unity, such that

$$4\pi \int_0^\infty r^2 \rho_1(r) dr = 1 \quad (6)$$

is the complete three-dimensional normalization integral over both electrons. In interparticle coordinates,  $\rho_i(r)$ , where  $i = 1$

or 2, is defined for a spherically symmetric state as

$$\begin{aligned} \rho_i(r) &= \langle \psi | \delta(r_i - r) | \psi \rangle \\ &= \int_0^\infty \int_0^\infty \int_{|r_1-r_2|}^{|r_1+r_2|} \delta(r_i - r) |\psi(r_1, r_2, r_{12})|^2 \\ &\quad \times 8\pi^2 r_1 r_2 r_{12} dr_{12} dr_2 dr_1, \end{aligned} \quad (7)$$

where  $8\pi^2 r_1 r_2 r_{12} dr_1 dr_2 dr_{12}$  is the volume element [13]. The electron-pair density or intracule function  $h(r)$  can also be defined for a two-electron system as

$$\begin{aligned} h(r) &= \langle \psi | \delta(r_{12} - r) | \psi \rangle \\ &= \int_0^\infty \int_0^\infty \int_{|r_1-r_2|}^{|r_1+r_2|} \delta(r_{12} - r) |\psi(r_1, r_2, r_{12})|^2 \\ &\quad \times 8\pi^2 r_1 r_2 r_{12} dr_{12} dr_2 dr_1. \end{aligned} \quad (8)$$

Recently [7], we showed that the single-electron density  $\rho_i(r)$  decreases monotonically whereas the intracule density  $h(r)$  contains a maximum which shifts to a greater distance as the charge of the nucleus decreases. In this work, the average electron-nucleus distances  $\langle r_1 \rangle$  and  $\langle r_2 \rangle$  are equal because the wave function is symmetrical in the two electrons, similarly  $\rho_1(r) = \rho_2(r)$ , etc. However, due to the electron repulsion, at any given instant one electron will be closer to the nucleus (an *inner* electron) than the other (an *outer* electron), and therefore an inner and outer component can be defined such that

$$\rho_1(r) + \rho_2(r) = \rho_{\text{in}}(r) + \rho_{\text{out}}(r). \quad (9)$$

Evaluating the Dirac  $\delta$  distribution in Eq. (7) leads to

$$\begin{aligned} \rho_1(r) + \rho_2(r) &= \int_0^\infty \int_{|r-r_2|}^{|r+r_2|} |\psi(r, r_2, r_{12})|^2 (2\pi r_2 r_{12}/r) dr_{12} dr_2 \\ &\quad + \int_0^\infty \int_{|r_1-r|}^{|r_1+r|} |\psi(r_1, r, r_{12})|^2 (2\pi r_1 r_{12}/r) dr_{12} dr_1, \end{aligned} \quad (10)$$

where the terms in parentheses arise from the reduced volume element. The integral range can then be split into an inner component ranging from 0 to  $r$ , where  $r$  corresponds to the radial distance of the electron farthest from the nucleus, i.e.,  $\max(r_1, r_2)$ , and an outer component ranging from  $r$  to  $\infty$ , where  $r$  corresponds to the radial distance of the electron nearest to the nucleus, i.e.,  $\min(r_1, r_2)$ . We can then define the inner component as

$$\begin{aligned} \rho_{\text{in}}(r) &= \int_0^r \int_{|r-r_2|}^{|r+r_2|} |\psi(r, r_2, r_{12})|^2 (2\pi r_2 r_{12}/r) dr_{12} dr_2 \\ &\quad + \int_0^r \int_{|r_1-r|}^{|r_1+r|} |\psi(r_1, r, r_{12})|^2 (2\pi r_1 r_{12}/r) dr_{12} dr_1, \end{aligned} \quad (11)$$

and the outer component as

$$\begin{aligned} \rho_{\text{out}}(r) &= \int_r^\infty \int_{|r-r_2|}^{|r+r_2|} |\psi(r, r_2, r_{12})|^2 (2\pi r_2 r_{12}/r) dr_{12} dr_2 \\ &\quad + \int_r^\infty \int_{|r_1-r|}^{|r_1+r|} |\psi(r_1, r, r_{12})|^2 (2\pi r_1 r_{12}/r) dr_{12} dr_1. \end{aligned} \quad (12)$$

TABLE I. Inner and outer expectation values (in atomic units) for the infinite nuclear mass helium isoelectronic sequence and for the critical nuclear charge system  $Z_C = 0.911\,028\,2(3)$  [7]. The inner electron mean radius is compared to that of a hydrogenic system  $\langle r_H \rangle = (\frac{3}{2Z})a_0$ .

System	$\langle r_{\text{in}} \rangle$	$\langle r_{\text{out}} \rangle$	$\langle r_1 \rangle$	$\langle r_H \rangle - \langle r_{\text{in}} \rangle$	$\frac{\langle r_H \rangle - \langle r_{\text{in}} \rangle}{\langle r_H \rangle} \%$	$\frac{\langle r_{\text{out}} \rangle - \langle r_H \rangle}{\langle r_H \rangle} \%$
$Z_C$	1.621 049 542	6.672 277 416	4.146 663 479	0.025 441	1.55	305.24
$\text{H}^-$	1.427 714 520	3.992 642 027	2.710 178 273	0.072 285	4.82	166.18
He	0.602 359 418	1.256 585 170	0.929 472 294	0.147 640	19.69	67.54
$\text{Li}^+$	0.380 512 965	0.765 035 334	0.572 774 149	0.119 487	23.90	53.01
$\text{Be}^{2+}$	0.278 005 362	0.550 561 293	0.414 283 328	0.096 994	25.87	46.82
$\text{B}^{3+}$	0.218 990 284	0.430 121 204	0.324 555 744	0.081 009	27.00	43.37
$\text{C}^{4+}$	0.180 638 705	0.352 949 031	0.266 793 868	0.069 361	27.74	41.18
$\text{N}^{5+}$	0.153 716 531	0.299 268 269	0.226 492 400	0.060 569	28.27	39.66
$\text{O}^{6+}$	0.133 777 666	0.259 765 875	0.196 771 771	0.053 722	28.65	38.54
$\text{F}^{7+}$	0.118 417 170	0.229 478 401	0.173 947 786	0.048 249	28.95	37.69
$\text{Ne}^{8+}$	0.106 220 610	0.205 517 570	0.155 869 090	0.043 779	29.19	37.01
$\text{Fm}^{98+}$	0.010 342 6757	0.019 770 292	0.015 056 484	0.004 657	31.05	31.80

Since the total electron density is rigorously partitioned into an inner and outer component, the analogous expression for the radial density function,  $D(r) = 4\pi r^2 \rho(r)$ , is  $D_1(r) + D_2(r) = D_{\text{in}}(r) + D_{\text{out}}(r)$ , and since  $D_1(r) = D_2(r)$  the one-particle radial density function for electron 1, say, is

$$D_1(r) = \frac{1}{2} \{D_{\text{in}}(r) + D_{\text{out}}(r)\}, \quad (13)$$

and similarly for any operator that depends only on the radial variable  $r$ . For example, the expected value for the inner component  $\langle r_{\text{in}} \rangle$  and the outer component  $\langle r_{\text{out}} \rangle$ , exploiting the fact that  $\langle r_1 \rangle = \langle r_2 \rangle$ , can now be defined as

$$\begin{aligned} \langle r_{\text{in}} \rangle &= 2 \int_0^\infty \int_0^{r_1} \int_{|r_1-r_2|}^{|r_1+r_2|} r_2 |\psi(r_1, r_2, r_{12})|^2 \\ &\quad \times 8\pi^2 r_1 r_2 r_{12} dr_{12} dr_2 dr_1, \\ \langle r_{\text{out}} \rangle &= 2 \int_0^\infty \int_{r_1}^\infty \int_{|r_1-r_2|}^{|r_1+r_2|} r_2 |\psi(r_1, r_2, r_{12})|^2 \\ &\quad \times 8\pi^2 r_1 r_2 r_{12} dr_{12} dr_2 dr_1. \end{aligned} \quad (14)$$

These equations also satisfy the relation  $\langle r_1 \rangle + \langle r_2 \rangle = \langle r_{\text{in}} \rangle + \langle r_{\text{out}} \rangle = 2\langle r_1 \rangle$ .

### III. METHOD

The Schrödinger equation, with the nucleus in motion and with the nucleus fixed, was solved for the singlet ground state  $^1S$  of two-electron atoms (with  $Z = Z_C$  [7] and  $Z = 1$ –10 and 100) by expanding the wave function in a triple orthogonal set of Laguerre functions in scaled perimetric coordinates [12–14]. The scaled perimetric coordinates used in this work are defined as

$$u = \alpha(r_2 + r_{12} - r_1), \quad (15)$$

$$v = \alpha(r_{12} + r_1 - r_2), \quad (16)$$

$$w = \gamma(r_1 + r_2 - r_{12}), \quad (17)$$

where  $r_1$  and  $r_2$  are respectively the distances of electrons 1 and 2 from the nucleus,  $r_{12}$  is the electron-electron distance, and  $\alpha$  and  $\gamma$  are nonlinear variational parameters optimized

for a given basis set size. A 2856 matrix was used throughout because this basis set size was found to be optimum in terms of computational effort for a given accuracy; for further method details see [7,15]. The finite nuclear mass  $M$  for the critical nuclear charge system  $Z_C$  was taken as the helium nuclear mass = 7294.299 536 1 [16]. The wave function was optimized using either 16-digit ( $\text{Be}^{2+}$  to  $\text{Ne}^{8+}$  and  $\text{Fm}^{98+}$ ) or 32-digit ( $\text{H}^-$  to  $\text{Li}^+$ ,  $Z_C$ ) precision, and the probability density functions and expectation values were all calculated using 32-digit precision. The inner and outer equations (11), (12), (14), etc., were transformed to perimetric coordinates (15)–(17) to eliminate the coupled integral range in  $r_{12}$  before evaluating.

## IV. RESULTS AND DISCUSSION

### A. Expected (mean) electron-nucleus distance in two-electron atoms

The expectation values of the electron-nucleus distance  $\langle r_1 \rangle$ , the inner electron  $\langle r_{\text{in}} \rangle$ , and the outer electron  $\langle r_{\text{out}} \rangle$  are provided in Table I for the helium isoelectronic series  $Z = 1$ –10 and 100, as well as the critical nuclear charge system  $Z_C = 0.911\,028\,2(3)$  [7] with infinite nuclear mass. The effect of nuclear motion is to increase the mean radii. For example,  $\langle r_{\text{in}} \rangle$  and  $\langle r_{\text{out}} \rangle$  for  $^4\text{He}$  are 0.602 443 and 1.256 772 and for  $^\infty\text{He}$  are 0.602 359 and 1.256 585, respectively. The differences are small however, and hence only the infinite nuclear mass data are presented.

The  $\langle r_{\text{in}} \rangle$  and  $\langle r_{\text{out}} \rangle$  data in Table I, considered accurate to at least seven significant figures (s.f.) for the anions and at least 11 s.f. for helium and the cations, are in excellent agreement with the limited data available in the literature for  $\text{H}^-$  to  $\text{B}^{3+}$  using numerical Hartree-Fock wave functions [6]. The correlated values presented by Koga for  $\text{H}^-$  to  $\text{B}^{3+}$  using multiconfigurational HF agree with the more accurate data in Table I to two–four s.f. and his HF values differ from the correlated values significantly as expected. The mean radius for both the inner electron and the outer electron decreases with increasing nuclear charge. The deviation of  $\langle r_{\text{in}} \rangle$  from  $\langle r_1 \rangle (= |\langle r_{\text{out}} \rangle - \langle r_1 \rangle|)$ , reduces from  $0.33a_0$  in helium to just  $0.05a_0$  in  $\text{Ne}^{8+}$ , whereas the deviation for the anion  $\text{H}^-$  is nearly 4 times greater than that in helium with a value of  $1.28a_0$  ( $0.679 \text{ \AA}$ ). The difference between the inner and outer radii

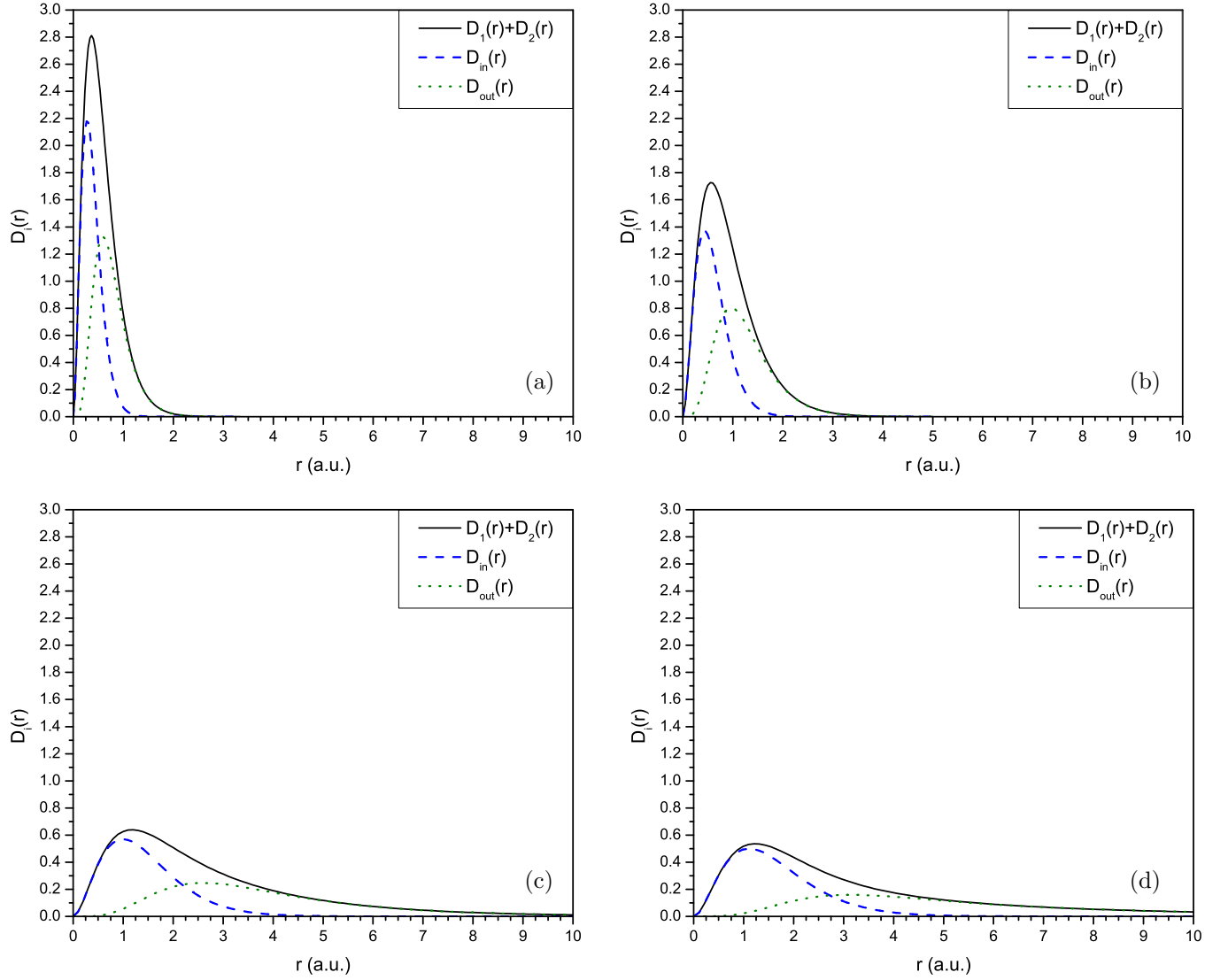


FIG. 1. Inner (blue/dash) and outer (green/dot) one-electron radial density functions of the total radial density function  $D_1(r) + D_2(r)$  (black/solid) in correlated two-electron systems: (a)  $\text{Li}^+$ , (b)  $\text{He}$ , (c)  $\text{H}^-$ , and (d) the critical nuclear charge system  $Z_c$ . The most probable radii,  $r_{\text{max}}$ , in the distributions for  $D_1(r) = D_2(r)$ ,  $D_{\text{in}}(r)$ , and  $D_{\text{out}}(r)$  are (a) 0.362, 0.278, 0.595, (b) 0.566, 0.437, 0.964, (c) 1.177, 0.996, 2.602, and (d) 1.232, 1.110, 3.135.

$|\langle r_{\text{out}} \rangle - \langle r_{\text{in}} \rangle|$  for the helium isoelectronic sequence ranges from just over  $2.5a_0$  in  $\text{H}^-$  to less than  $0.1a_0$  in  $\text{Ne}^{8+}$  ( $1.36$ – $0.05$  Å). However, at the critical nuclear charge for binding, the difference is over  $5a_0$  ( $2.67$  Å), a surprisingly large radial distance for this singlet state.

Also included in Table I is the difference between the hydrogenic (one-electron system) mean radius  $\langle r_{\text{H}} \rangle$  and the inner mean radius  $\langle r_{\text{in}} \rangle$  of a fully correlated two-electron system. The results show that in all cases the electron-electron repulsion works to shift the inner electron toward the nucleus and the outer electron away from the nucleus relative to the hydrogenic values. Interestingly, the maximum absolute perturbation occurs for the neutral helium atom. For weakly bound systems the excess of negative charge means that the electrons must distribute themselves far away from each other to minimize electron repulsion. For cationic species (i.e., strongly bound systems) the nucleus-electron attraction energy dominates over the electron-electron repulsion, and both the

absolute inner and absolute outer mean radii indicate that both electrons are close to the nucleus. However, the data suggest that the inner electron is always closer to the nucleus than a one-electron system and the outer electron is always farther from the nucleus. To test whether the outer electron mean radius converges on the hydrogenic value, a calculation was performed on  $\text{Fm}^{98+}$ . The percentage difference between the mean radius for the hydrogenic system  $\text{Fm}^{99+}$  and the inner mean radius of  $\text{Fm}^{98+}$  is 31.05%, and the difference between the outer mean radius and the hydrogenic system is 31.80%. This indicates that within the nonrelativistic limit, even at very high charge the outer electron experiences a reduced effect of the nucleus due to the presence of the repulsive inner electron.

## B. Radial density functions

The radial probability density function  $D(r)$  provides greater detail on the radial distribution of individual electrons

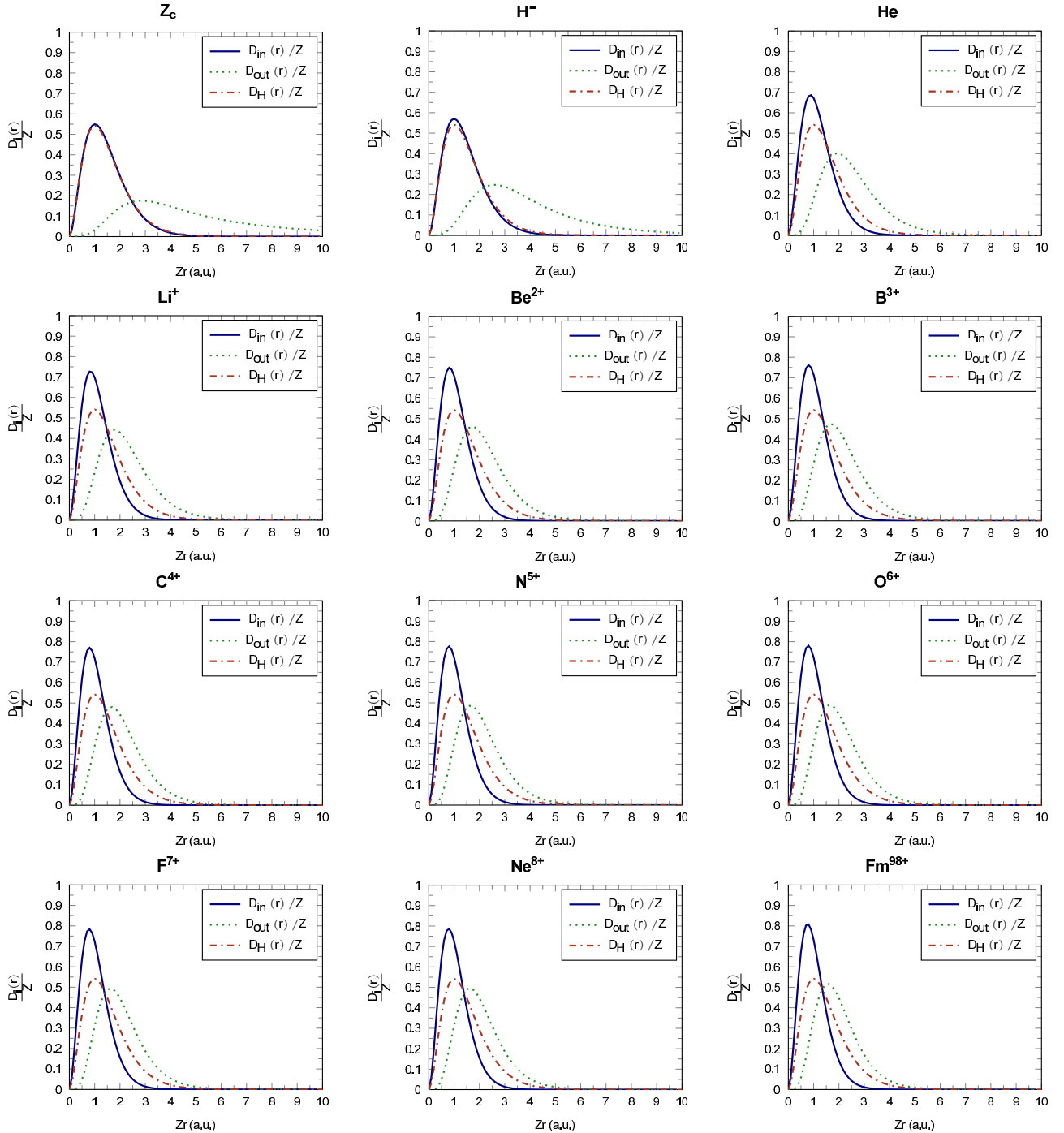


FIG. 2. Comparison of the  $Z$ -scaled (normalized) inner and outer electron radial density functions,  $D_{\text{in}}(r)$  (blue/solid) and  $D_{\text{out}}(r)$  (green/dots), with  $D_{\text{H}}(r)$  the radial distribution of its hydrogenic equivalent (red/dot-dash), in correlated two-electron systems.

in two electron systems, including the most probable radius  $r_{\text{max}}$ . The inner and outer radial density functions  $D_{\text{in}}(r)$  and  $D_{\text{out}}(r)$ , respectively, represent the probability that one electron moves with a radius  $r$  which is smaller than the radius of the other electron, and the probability that one electron moves with a radius  $r$  which is greater than the radius of the other electron, in a fully correlated two-electron system.

The radial density functions are presented in Fig. 1 for  $\text{Li}^+$ ,  $\text{He}$ ,  $\text{H}^-$ , and  $\text{Zc}$ . In each case,  $D_1(r) + D_2(r)$  is partitioned into

an inner  $D_{\text{in}}(r)$  and an outer  $D_{\text{out}}(r)$  electron distribution. They indicate that when  $Z \geq 2$ , the electrons remain localized close to the nucleus, as the greater nuclear charge compensates for the electron repulsion between the two electrons. However, when  $Z < 2$ , the total radial density function is much more diffuse; the inner electron distribution remains reasonably localized whereas it is the outer electron distribution that gives the total radial density function its highly diffuse character. This can be seen by the shift of the maximum in the probability density  $r_{\text{max}}$  to greater values of  $r$  and the diffuse tail in the



total radial density function that can be attributed to the outer electron, Figs. 1(c) and 1(d).

To quantify the localization of the inner electron,  $D_{\text{in}}(r)$  is compared with the corresponding hydrogenic radial distribution function. The radial density functions for  $Z_C$ ,  $Z = 1-10$ , and  $Z = 100$ , are shown in Fig. 2, scaled by  $Z$  to facilitate direct comparison between systems [17]. It is clear that the inner radial density function remains localised for all systems and, particularly for the systems with  $Z < 2$ , can be modelled reasonably accurately as a perturbed one electron system (Fig. 2). Significantly, the inner electron distribution becomes more hydrogenic-like as the nuclear charge decreases to the extent that there is very little discernible difference between the distribution for the hydrogenic system and that calculated as the inner electron distribution of a weakly bound two-electron system. Conversely, for helium and the cationic systems, the inner radial density function of the correlated system is more localized around the nucleus ( $r_{\text{max}} < (1/Z)a_0$  and the distribution more contracted) than that of the hydrogenic analogs. The inner electron experiences what Hylleraas describes in [2], p.109, as a *negative screening* effect due to the presence of a second electron, whereby the effective nuclear charge of the inner electron is greater than  $Z$  due to the presence of the outer electron, which experiences a reduced effect of the nucleus.

This further supports the comparison of  $\langle r_{\text{in}} \rangle$  with the hydrogenic expectation values provided in Table I. It appears that the Coulombic repulsion from the outer electron results in the inner electron moving closer to the nucleus. This can be represented as an increase in the effective charge experienced by the electron [ $Z_{\text{eff}} = 1.004$  for  $\text{H}^-$  and 2.288 for  $\text{He}$ , obtained by fitting  $D_{\text{in}}(r_{\text{max}})$  to  $(1/Z)a_0$ ]. This is a direct consequence of the perturbing effect of the second electron. While the effect for the hydride ion is quite small, the inner electron of the more compact helium atom experiences a greater negative screening; and as the charge increases, the difference between  $Z$  and  $Z_{\text{eff}}$  for the inner electron also increases (e.g., for  $\text{Li}^+$ ,  $Z_{\text{eff}} = 3.597$ ). The  $Z$ -scaled profile of the inner electron, relative to the corresponding hydrogenic profile, is very similar for all  $Z$  greater than about 6, and in all cases the inner electron distribution is considerably more localized (less diffuse) than the hydrogenic equivalent. The effect of increasing nuclear charge simply results in the outer electron moving closer to the nucleus by overcoming the electron repulsion more effectively.

Experimental evidence for one very weakly bound electron and a localized hydrogenic system in the hydride ion can be observed in experimental ionization energies (IEs). The calculated ionization energy of the two-electron system is simply the difference between the fully correlated ground-state energy and the hydrogenic energy, which for an infinite nuclear mass system is  $-Z^2/2$  and for a finite nuclear mass system is  $-Z^2M/2(1+M)$ . Using the conversion 1 a.u. = 27.211 385 05 eV [16], the first and second ionization energies of the nonrelativistic hydride ion, with an infinite nuclear mass, are 0.755 14 and 13.605 eV, respectively, and for a finite nuclear mass are 0.754 246 and 13.5982 eV in good agreement with experimental values of 0.754 593 [18] and 13.5984 eV [16]. The second ionization energy is approximately 18 times larger than that of the first, indicating a

very weakly bound outer electron. In contrast, for helium the calculated ionization energies with an infinite nuclear mass, 24.591 and 54.422 eV, and a finite nuclear mass, 24.587 and 54.415 eV, are in very good agreement with experimental values 24.587 387 94 [19] and 54.417 763 11 eV [16], and the second ionization is approximately double that of the first. These physical properties are explained by the localization of the He outer electron [Fig. 1(b)] compared to the diffuse nature of the outer electron in the hydride radial distribution function [Fig. 1(c)].

The critical nuclear charge system  $Z_C$  has the minimum charge required for at least one bound state and so provides insight into the behavior of a system just prior to electron detachment. This is an important phenomenon and key to many chemical processes such as bond formation and ionization. Figures 1(d) and 2 ( $Z_C$ ) indicate that prior to chemical transformation in a two-electron atom, one electron remains very localized around the nucleus, behaving almost exactly like a one-electron system, while the interacting electron, the one taking part in a chemical process, becomes extremely delocalized with reduced nuclear-electron attraction driven by minimization of electron repulsion, which results in diminished radial correlation effects.

## V. CONCLUSIONS

In this paper we have shown that it is possible to separate the motions of two electrons in a fully correlated two-electron system by defining an *inner* electron which is on average closer to the nucleus at any instant, and an *outer* electron which is farther away from the nucleus than the other electron at any given instance. It is shown that the sum of the two one-electron radial operators equals the sum of the inner and outer components, and that this relation is satisfied by any operator that depends only on the radial variable  $r$ . In the present work, the particle density  $\rho(r)$ , radial probability density function  $D(r)$ , and the expectation value of the interparticle distances  $\langle r \rangle$  have all been considered. The results presented show that in all cases (for cationic, neutral, and anionic systems) the inner electron experiences a negative screening effect due to the perturbation by the other electron. The balance of the nuclear-electron attraction and the electron-electron repulsion determines the magnitude of  $|\langle r_{\text{in}} \rangle - \langle r_{\text{out}} \rangle|$ .

It is shown that for the helium isoelectronic series ( $Z \geq 2$ ), the most probable distance ( $r_{\text{max}}$ ) of the inner electron is always closer to the nucleus, and that of the outer electron always farther away from the nucleus, than the most probable distance in the corresponding one-electron (hydrogenic) system. Furthermore, the inner electron is more localized and less diffuse than that of a hydrogenic system, whereas the converse is true for the outer electron. As the nuclear charge increases ( $Z \geq 6$  or 7), the  $Z$ -scaled inner electron radial density function does not change substantially. The effect of the increase in the nuclear charge is for the outer electron to move closer to the nucleus. However, due to electron repulsion, the most probable distance of the outer electron never becomes less than that of the hydrogenic system, and even at  $Z = 100$  the (nonrelativistic) outer electron distribution is more diffuse than the inner electron distribution but quite similar to that of

the hydrogenic system (just shifted slightly along the  $Zr$  axis away from the nucleus).

For the weakly bound anionic systems ( $Z \leq 1$ ) the inner electron distribution closely resembles that of the corresponding hydrogenic system with the radial density distribution of the outer electron becoming very diffuse as the charge decreases. In this paper we have quantified the radial correlation effects of two electrons close to electron detachment, revealing

the significant magnitude of the mean radius of the detaching electron (over 6 a.u.), by studying the critical nuclear charge system.

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